

The Examiner's Action mailed September 11, 2001 (Paper No. 4) and the references cited therein have been carefully studied by Applicants and the undersigned counsel. The amendments appearing herein and these explanatory remarks are believed to be fully responsive to the Action. Accordingly, this important patent application is believed to be in condition for allowance.

Relying on 35 U.S.C. §112, second paragraph, the Office has rejected the subject matter of claims 1-8 as being indefinite for failing to particularly point out and distinctly claim the subject matter which Applicants regard as the invention. The Examiner alleges that it is unclear what Applicants intend by the limitation "lowered metal silica produced from silicate ester." Applicants respectfully traverse the rejection and request reconsideration.

Applicant submits that claims 1-8 are originally presented and herein presented as claims 9-16 do define the legal metes and bounds of the invention. It is not the role of the claims to enable one skilled in the art to reproduce the invention but rather to define, for those skilled in the art the legal metes and bounds of the invention.

It is well known before the present application that high purity silica sol is produced from silicate ester. This is also described in the reference cited by the Examiner. Further, the "Quartron PL-10" sold by the applicant is produced from silicate ester as described in the attached copy of a FUSO CHEMICAL CO. pamphlet (Document 1). Therefore, those skilled in the art can easily understand a description such as "lowered metal colloidal silica produced from silicate ester", and the description of the claim is not unclear.

It is respectfully submitted that original claims 1-8 did, and new claims 9-16 also fully comply with 35 U.S.C. §112, second paragraph. Withdrawal of the rejection is respectfully requested.

Relying on 35 U.S.C. §102(b), the Examiner has rejected the subject matter of claim 1 as being anticipated by Payne ('431 patent). Applicants respectfully traverse the rejection and request reconsideration.

Applicant respectfully submits that it is important to note that, historically, the Office and the Federal Circuit has required that for a §102 anticipation, a single reference must teach (i.e., identically describe) each and every element of the rejected claim. The Office has steadfastly and properly maintained that view.

The '431 patent fails this test. Applicants herein incorporate by reference the attached Rule 132 Declaration. The referenced '431 patent does not disclose a composition with the limitation "pH from 6.0 to 8.0." Accordingly, each and every element of Applicants' claim have not been taught in that single reference. In other words, the rejected claims do not read literally on any single item of prior art because the '431 patent does not teach, disclose or suggest the pH limitation claimed in new claim 9. Accordingly, Applicants respectfully submit that claim 9 has not been anticipated by the '431 patent under 35 U.S.C. §102(b), and respectfully request that such rejection be withdrawn.

Relying on 35 U.S.C. §103(a), the Examiner has rejected the subject matter of claims 1-8 as obvious over Romberger ('833 patent), in view of the '431 patent. Applicants respectfully traverse the rejection and request reconsideration.

It is evident that Applicants' invention is decidedly different from the teachings of the cited references. Applicants herein incorporate by reference the attached Rule 132 Declaration executed by one of the inventors herein, Masatoshi SAKAI (see document 5).

In summary, the present invention is characterized that the colloid silica slurry wherein hydrogen peroxide from 5 to 100 ppm is added and pH is from 6.0 to 8.0. On the other hand, in the '833 patent, lowered metal silica slurry used in polishing of silicon wafer is described, and it is described that lowered metal silica can be produced from the silicate ester. In columns 3 and 4, related to the "BACKGROUND OF THE INVENTION", it is described that "in US Patent No. 3,860,431, hydrogen peroxide is used as biocide". In US Patent No. 3,860,431 (Payne et al), an invention which relates to slip resistant composition for paper coating is described. In lines from 50 to 63 of Col. 4, hydrogen peroxide is exemplified as a kind of biocide. In lines 64 to 66 of the Col. 4, it is described from 0 to 0.5 %, preferably from 0.3 to 0.5% as composition quantity of biocide.

Hydrogen peroxide is also exemplified as biocide in the '833 patent. Although hydrogen peroxide is disclosed as an example in '431, hydrogen peroxide cannot be used as a biocide in an invention which relates '431. That is, in lines from 13 to 14 of Col. 3 of the '431 patent, the use of alkaline silica sols is disclosed, and pH of Silika Sol A to D exemplified in Table 1 of Col. 3 is from 8.6 to 10.0. Further, in Composition W~Z actually prepared in the column example of the '431 patent, in an invention which relates to the '431, alkaline silica sol is used. In the '431 patent, hydrogen peroxide is exemplified as a biocide, under alkaline conditions, but in the invention which relates to the '431 patent, hydrogen peroxide decomposes very easily, that is, it can not be used as a biocide.

It is clear from result of a test example described in the attached declaration, that hydrogen peroxide easily decomposes under alkaline conditions. That is, when hydrogen peroxide was added in colloidal silica where pH was maintained in a neutral zone, resolution of hydrogen peroxide was hardly confirmed even it had been maintained 12 days at 40 centigrade.

On the other hand, when hydrogen peroxide was added to commercially available colloidal silica where pH was prepared in an alkaline zone, in particularly pH was adjusted in 9.6 or 9.2 and maintained under same condition, about 66% and 42% resolution of hydrogen peroxide was confirmed.

Therefore, in the '431 patent, even though hydrogen peroxide is exemplified as a kind of biocide, it is understood that in an invention which relates to the '431, hydrogen peroxide actually cannot be used as biocide. Even if hydrogen peroxide is used as biocide in the invention which relates to '431, hydrogen peroxide decomposes and it does not work as a biocide. Further, when a person composes hydrogen peroxide with the knowledge of its resolution, he or she needs to compose a large quantity of hydrogen peroxide. Existence of a large quantity of hydrogen peroxide involves a risk of causing corrosion to metal in keeping or using. The attached literature herein from Chemical Industries Association, entitled "Chemical Device Manual" dated June 15, 1970, Maruzen Co., Ltd. pages, 507, 518 and 519 (see Document 2 and Document 3, which is a translation of a substantial portion of Document 2), also describes that hydrogen peroxide has a risk of causing corrosion to metal.

Based on the fact that hydrogen peroxide is not actually used in any EXAMPLE in the '431 patent, it is clear that hydrogen peroxide cannot be used as biocide in an invention which relates to '431. Further, in an invention which relates to the invention '833 which cites the description of the '431 patent, in lines from 34 to 35 of Col. 8 of the '833 patent, pH of colloidal silica is described as alkaline from 8.5 to 11.3. Hence it is understood that in an invention according to the '833 patent, hydrogen peroxide cannot be used as biocide.

Therefore, in the inventions as disclosed in the '431 and '833 patents, although hydrogen peroxide is impliedly described as being able to be used as biocide of silica sol, in fact, hydrogen peroxide actually cannot be used as biocide.

**By using hydrogen peroxide as biocide, the present invention has superior effect as described below.**

First, the present invention works as biocide with a very small composition quantity, that is, a small composition quantity which does not involve risk of corrosion by hydrogen peroxide at all. In the present invention, a composition from 5 to 100 ppm is enough. It is clear from the result of the test example in the specification of the present application, that it can gain enough effect with adding a small composition quantity hydrogen peroxide. In another biocide, for example, glutaraldehyde, 0.5% is needed to be composed. The reason that composition quantity of hydrogen peroxide is from 5 to 100 ppm is that when the composition quantity is less than 5 ppm, hydrogen peroxide does not work as biocide, and when hydrogen peroxide is composed over 100 ppm, there is a risk of corrosion to metal in keeping or using. This is not preferable.

Second, when colloidal silica slurry is used as polishing agent slurry, it is used with an added conditioner such as acid or alkaline medical agent, oxidizing reagent and detergent. Where it is used with mixing with another conditioner, it is preferable that pH be from 6.0 to 8.0. Also, at this limit, environmental pollution is minimized.

Third, when hydrogen peroxide is used as biocide, it has no effect on average particle diameter or pH value, and it is superior to preserving stability. This is figured out from the result of the test example in the specification in application.

Further, by keeping metal in colloidal slurry 1 ppm, when colloidal slurry which relates to the present invention is used as polishing agent, a defect such as scratching does not occur. When

impurities content is over 1 ppm, it has the possibility that defects can occur such as scratching after polishing. Applicants herein attach a Translation of a substantial part of the Chemical Industries Association literature mentioned above. Applicants further attach a fourth document entitled "Current status and future plan of practical application of CMP in mass production line: dated January 31, 1997, pages 7-18, issued by Science Forum, Inc. (See Document 4).

As explained above, in the colloidal slurry described in '431 and '833, hydrogen peroxide cannot be used practically as biocide. Hence, in '431 and '833, the use of hydrogen peroxide as a biocide of colloidal silica slurry is really not actually described. Further, by using hydrogen peroxide, the present invention has superior effect as mentioned above. Therefore, the present invention is an invention which has an inventive step and is unobvious.

Accordingly, the Examiner has not established a prima facie case of obviousness.

Clearly, there is an absence of any suggestion or any teaching whatsoever of how one skilled in the art would attempt to combine the cited references to arrive at the present invention.

The Office has used the claimed invention as a reference against itself as if it had preceded itself in time. Legal authority invalidates such an analytical or reverse engineering approach to patent examination. It is not Applicants' burden to refute the Office's position that it would have been obvious to one of ordinary skill in this art at the time this invention was made to arrive at the present invention in view of the cited patents. It is the burden of the Office to show some teaching or suggestion in the reference to support this allegation. Uniroyal, Inc. v. Rudkin-Wiley Corp., 837 F.2d at 1051, 5 U.S.P.Q.2d at 1438-39 (Fed. Cir. 1988).

A finding by the Office that a claimed invention would have been obvious to one of ordinary skill in the art at the time the invention was made based merely upon finding similar elements in a prior art reference would be "contrary to statute and would defeat the congressional

purpose in enacting Title 35." Panduit Corp. v. Dennison Mfg. Co., 1 U.S.P.Q.2d 1593 at 1605 (Fed. Cir. 1987). Accordingly, Applicants respectfully submit that original claims 1-8, which are herein replaced with new claims 9-16, are patentable over the cited patents under 35 U.S.C. §103(a). Withdrawal of the rejection is respectfully requested.

In a recent case before the Circuit Court of Appeals for the Federal Circuit decided on May 13, 2002, the court found that a prior art reference will NOT be assumed to inherently contain claimed property because it discloses same structure. The plaintiff in the case was attempting to have the court declare defendant's patent invalid as obvious over a prior art patent that disclosed the same structure but did not specifically disclose a 2 percent limitation for reduction of a reflection contribution. Plaintiff argued that the limitation was inherently there because the basic structure was the same. Plaintiff had not shown that the prior art taught, suggested or motivated the reduction to about 2 percent. Crown Operations International Ltd. v. Solutia Inc., 62 USPQ2d 1917 (Fed. Cir. 2002).

In the instant application, the cited references are being in effect used by the Examiner as disclosing its alleged inherent limitations, when no support exists in the cited references to use hydrogen peroxide as a biocide. Therefore, it is improper to inherently extend these references to the present invention as claimed.

### CONCLUSION

As the Federal Circuit observed in Orthopedic Equipment Co. v. United States, 702 F.2d 1005, 217 U.S.P.Q. 193 (Fed. Cir. 1983):

The question of nonobviousness is a simple one to ask, but difficult to answer ... The difficulty which attaches to all honest attempts to answer this question can be attributed to the strong temptation to rely on hindsight while undertaking this evaluation. It is wrong to use the patent in suit as a guide through the maze of prior art references, combining the right references in the right way so as to

achieve the result of the claims in suit. Monday morning quarterbacking is quite improper when resolving the question of nonobviousness ...


Even though the initial claims in this important patent application were drawn to a new, useful and nonobvious invention, they have now been canceled and replaced with new claims 9-16.

A Notice of Allowance is earnestly solicited.

If the Office is not fully persuaded as to the merits of Applicant's position, or if an Examiner's Amendment would place the pending claims in condition for allowance, a telephone call to the undersigned at (727) 538-3800 would be appreciated.

Very respectfully,

Dated: 2/4/03

  
Dennis G. LaPointe  
Mason Law, P.A.  
17757 U.S. Hwy. 19 N., Suite 500  
Clearwater, FL 33764  
(727) 538-3800  
Reg. No. 40,693



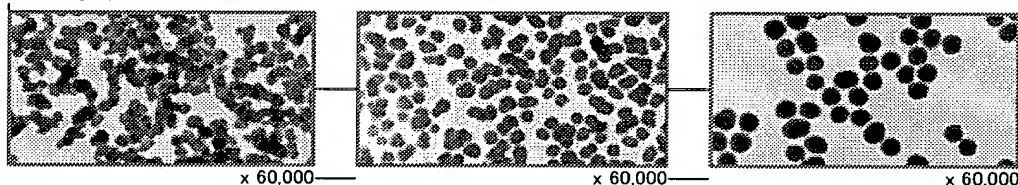
Quatron PL Series High Purity Colloidal Silica



**Characteristics**

This product is high purity colloidal silica prepared by particle growth method using hydrolysis and condensation with high purity alkoxysilane as a starting material.  
Compared with colloidal silica starting from sodium silicate, this product is more pure, spherical shaped and stable at neutrality.  
—The purity of the product excluding nonionic and ionic dispersing agent is 99.99999% or more.  
Based on customer's requirement, it's possible to control particle size, degrees of the particle shape and select the dispersing agent, water, alcohol, glycol, etc.

Photographs of PL Series



**Properties**

The representative grades with water as the dispersing agent are shown below.  
—Depending on the customer's needs, the grades can be adjusted in particle size, particle shape, solvent, etc.

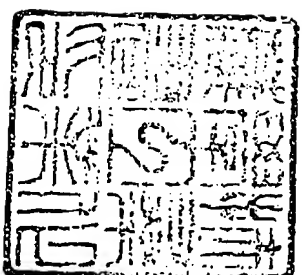
	items	unit	PL-1	PL-3	PL-7	PL-30
General	Appearance	—	slightly opal.	opalescent	milky	milky
	Specific gravity (20/4°C)	—	1.07	1.12	1.12	1.18
	pH	—	7	7	7	7
	Silica concentration	%	12	20	20	30
Particle size	Primary size (d1)	nm	15	35	70	300
	Secondary size (d2)	nm	40	70	120	360
	Aggregate ratio (d2/d1)	—	2.7	2.0	1.7	1.2
Impurities	Alkali metals	ppb	<300	<300	<300	<300
	Heavy metals	ppb	<100	<100	<100	<100

**Applications**

ICMP for IC planarization, Polishing of silicon wafers, Various fillers for coatings, etc.

# 化学装置便覧

化学工学協会編



丸善株式会社

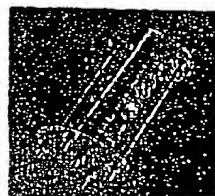


図 B-6-16 ステールホルダー内の一例

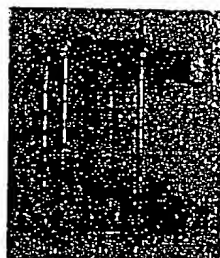


図 B-6-17 ステールホルダー内配付け状況の一例



図 B-6-18 配管用保持具 (I)

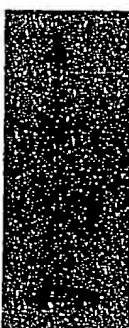


図 B-6-19 配管用保持具 (II)

ある。

これらの保持具による試験片の設置の際は、静止液中では試験片が垂直になるようにして、腐食生成物が他の試験片に影響しないようにする。また流動液中では流れ方向に平行になるように設置し、すべての試験片が液の流動に逆らわないようにする。

主として耐腐性を目的とする金属、めっき、塗装などの実地試験は、試験片を自然の大気中に放置する大気暴露試験にて行う<sup>11)</sup>。

標準的暴露試験台の例を図 B-6-20 に示す。これによって、実用条件にもっとも近い状態での耐腐性試験が行えるが、判定は長時間を要する。

以上述べた種々の実験室試験と実地試験を有効に駆使し、この結果に対して適当した判断を下すことによって最適な装置材料を選定することができる。



図 B-6-20 暴露試験台

## 6.2 耐食材料選定用資料

化学工業において、各種の腐食環境に対する耐食材料の選定は単に腐食だけの問題でなく、腐食生成物による着色、反応阻害など製品への影響もあるので、選定に当たっては十分な検討が必要である。

以下に示すデータ集は単に材料の予備的選択に役立つものであり、多数の影響因子を含んでいる実際の場合には、構造材料および使用薬品の実態をよくつかんだ上で最終決定の段階にはいるべきであると考ええる。

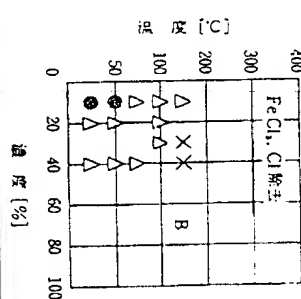
### 6.2.1 腐食データ集<sup>(9-11)</sup>

腐食データ集には二つの形がある。その一つは、腐食性物質の濃度、温度に対する材料の腐食度、または適、不適の格付けを整理編集したものと、他の一つは構造材料に対してデータを整理したものである。前者はユーザーに、後者はメーカーにとって便利である。ここではユーザー側から便利な環境別に分類整理する形式をとった。

腐食データ集を表 B-6.4 に、材料成分を表 B-6.3 に示す。

図 B-6.21 は表 B-6.4 の使い方を説明したもので、横軸に 0, 20, ……100% の濃度を、縦軸に 400°C までの温度をとっている。とくに使用ひん度の高い 100°C 以下では 50°C 目盛を使用しているので注意を要する。耐食性の判定基準は表に示したとおりである。

記入例は塩酸環境 (脱気,  $\text{FeCl}_3$ , Cl) を溶液中より除去) に対するハステロイ B の耐食性を示している。環境に対するハステロイ B は低温、低濃度で「完全耐食」、高温 (>150°C)、高濃度では「耐食性なし」、その中間の温度、濃度条件では「耐食性あり」、ただし使用するに当たっては十分な防食管理を必要とすることを表わしている。耐食性の判定基準は金属材料の場合には図 B-6.21 のとおりであるが、有機材料の場合には具体的な判定基準<sup>(16)</sup> が確立されておらず、重量、かさ、そのほかの変化を総合して判定しているのが現状である。



記号	受食度 [mm/yr]	飼 考
●	0.05 以下	完全耐食 耐食性あり ただし使用に当たって は要注意
△	0.05~1.00	
×	1.00 以上	耐食性なし

図 B-6.21 耐食変例 (塩酸に対するハステロイ B) および耐食性判定基準

表 B-6.3 材料の成分

材	料	C	Cr	Ni	Mo	Cu	Si	Fe	その他
18-8 ステンレス鋼 <sup>11)</sup>	SUS 304	<0.08	18~20	8~11				Bal.	
	SUS 316	<0.030	18~20	9~13				Bal.	
Mo ステンレス鋼 <sup>11)</sup>	SUS 321	<0.08	16~18	10~14	2~3			Bal.	Mo < 2
	SUS 33	<0.030	16~18	12~16	2~3			Bal.	Mo < 2
20 7 0 4	ステンレス鋼	<0.07	20	24	3	1.75	3.25	Bal.	Mo < 0.6
	ステンレス鋼	<0.07	19~21	28~30	3	4	1	Bal.	
イソコネル	ステンレス鋼	<0.15		67					
	ステンレス鋼	<0.08	15	77			0.25	7	Mn 0.25
ハステロイ	ハステロイ B	<0.12		60~65	25~30				
	ハステロイ C	<0.15	13~16	55~60	13~19				
ハステロイ D	ハステロイ D	<0.12	<1	Bal.					
	ハステロイ D	<0.12							

(注) 「シ」は通常炭素添加量を指し、材料の場合には表中に表記してある。

### 6.2.2 代表的薬品についての材料の選定

通常使用されている代表的薬品を取上げ薬品濃度、温度別に適当な耐食材料を選定する。耐食性の判定基準は侵食度 0.05 mm/yr 以下のものを「完全耐食」、1 mm/yr 以上のものを

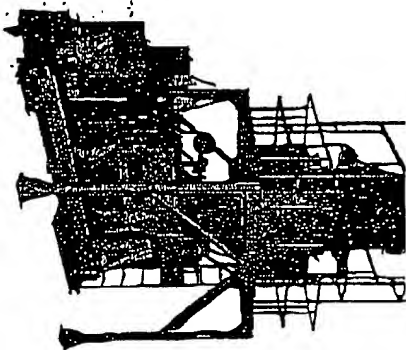


## 大和の重袋用全自動包装装置

包装およびこれに伴なう荷役作業の合理化が叫ばれ、深刻化してきた人手不足によって、設備の省力化、合理化が一段と注目されるに至りました。そこで、これらユーザー各位のご要望に応え、開発されたのが重袋用全自動包装装置です。

## 特 長

1. カム式のため、操作が正確で経年的な変化がない。給袋、袋位置決め、空袋移動、開口、充填シュー卜の下降、充填、袋形の一定の動作はカム機構で、タイミングスルなどの誤動作がない。また、カムに調整設定を行えば、その後の調整は必要なく、表面処理された鋼材であるため磨耗の心配もない。



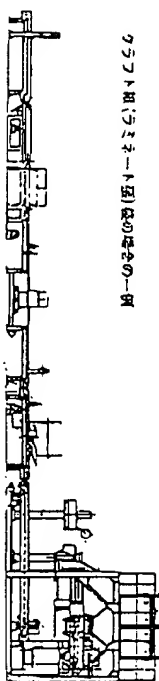
重袋用全自動包装装置

2. 給袋の位置でホジショニングするため、ミスがない。従来のミスの原因であった袋装差の不正確を、給袋の位置で位置決めするため、正確な口廻りができ、ミソノ隙もきれいに仕上がる。また送袋シュー卜も袋変形投入装置の動作は同一の速度モーターで駆動しており、袋変形、ミソが正確で袋の荷重が大きい。操作としては理想的なタイマーである。
3. 電気装置が少なく、故障が少ない。操作がカム式であるため、電気装置が少なく、自動機としては理想的なタイマーである。
4. 安全装置が付いている。ローソ式のため安全装置として予報緊急停止の装置が完備している。
5. 防塵対策ができていて、充填シュー卜が2重になっており、吸引ノズルを排気することにより、粉塵が外部へ流れないようにになっている。

## 仕 様 の 一 例

測定範囲	20~40kg	計量型式	FC-4, FC-4 VR 型など計量物の性状により決定する。
精 度	±1/500~1/1000		
能 力	700~800 袋/時		

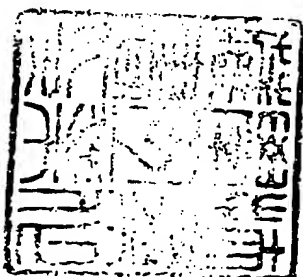
クラフト紙シュー卜型(袋)装のときの一例



## 大和製衡株式会社

本社・工場 〒673 兵庫県明石市茶園5-22 電話 (078) 912-2222 (大和)  
東京事務所 〒100 東京都千代田区丸の内野船ビル 電話 (03) 261-4757~9

## 化学装置便覧



¥ 6,000

昭和45年6月15日発行

© 1970

出 版 者 社団法人 化学工学協会

発 行 者 大 和 製 衡 有 限 公 司

発 行 所 大 和 製 衡 有 限 公 司

印刷所の所在地  
〒100 東京都千代田区丸の内野船ビル

印刷番号 100 東京都千代田区丸の内野船ビル

印刷 大和製衡株式会社・東京 株式会社 大和

# **Chemical device manual**

Editing by Chemical Industries Association

Maruzen Co., Ltd.

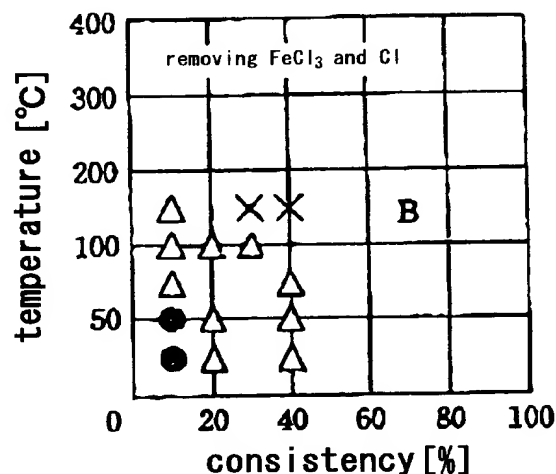
### 6·2·1 Corrosion data <sup>13-15)</sup>

There are two forms of corrosion data aggregation. One is edited concentration of corrosive substance, penetration, of material to temperature and rating of eligibility and ineligible, and the other is to gather data to composition material. Former is useful to user and latter is useful to corporation. In this text, the corrosion data aggregation is taken form of editing by circumstance for useful to user.

The corrosion data aggregation is shown in Table B·6·4, and material component is shown in Table B·6·3.

Figure B·6·21 explains usage of the Table B·6·4, and a horizontal axis shows concentration of 0, 20 ...100%, and a longitudinal axis shows temperature up to 400 centigrade. Please be careful that under 100 centigrade which is especially used, a mark which shows 50 centigrade is used. A criterion of corrosion resistance is as shown in the Table.

An example of entering shows corrosion resistance of Hastelloy B to hydrochloric acid circumstance (deaeration, FeCl<sub>3</sub> and Cl are removed from solution). Hastelloy B to the circumstance is "perfect anticorrosion" at low temperature and low concentration, "non corrosion resistance" at high temperature (>150) and high concentration and "corrosive resistant" in intermediate temperature and concentration. However, it shows that steadily corrosion prevention is necessary in use. In metal material, criterion of corrosion resistance is as shown in Figure B·6·21, but in organic material, practical criterion <sup>16)</sup> is not established, and in the present circumstance, weight, hardness and other change are evaluated in a comprehensive.



symbol	penetration [mm/yr]	comment
●	0.05 以下	perfect anticorrosion
Δ	0.05~1.00	corrosive resistant (behold in using)
x	1.00 以上	non corrosion resistance

Figure B 6·21 Table example of corrosion resistance (Hastelloy to hydrochloric acid) and criterion of corrosion resistance

Table B6·3 Component of material

Materials		C	Cr	Ni	Mo	Cu	Si	Fe	other
18-8 stainless steel <sup>17)</sup>	SUS 27	<0.08	18~20	8~11				Bal.	
	SUS 28	<0.030	18~20	9~13				Bal.	
Mo stainless steel <sup>18)</sup>	SUS 32	<0.08	16~18	10~14	2~3		<1	Bal.	Mn <2
	SUS 33	<0.030	16~18	12~16	2~3			Bal.	Mn <2
20 alloy	warsite durimet 20	<0.07	20	24	3	1.75	3.25	Bal.	Mn <0.6
		<0.07	19~21	28~30	3	4	1	Bal.	
Monel metal	Monel	<0.15		67		Bal.			
Inconel		<0.08	15	77		0.2	0.25	7	Mn 0.25
Hastelloy	Hastelloy B	<0.12		60~65	26~30				
	Hastelloy C	<0.15	13~16	55~60	15~19				
	Hastelloy D	<0.12	<1	Bal.		3.8~4.25	8.5~10		

(annotation) usually, natural vulcanizing gum is used as 「gum」, and when other gum is used, it is described in the tables.

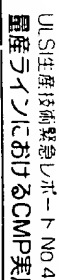
(Table B-6.4 continuation)

chemicals	Iron and steel		Stainless steel			Nickel	
	18-8 stainless steel (17)	Mo stainless steel (18)	20 alloy	Monel	Inconel		
sodium chlorate $\text{NaClO}_3$							
sodium perchlorate $\text{NaClO}_4$							
hydrogen peroxide $\text{H}_2\text{O}_2$							
potassium permanganate $\text{KMnO}_4$							
ammonium formate $\text{NH}_4\text{CO}_2$							
potassium chromate $\text{K}_2\text{CrO}_4$							
copper acetate $\text{Cu}(\text{CH}_3\text{COO})_2$							
lead acetate $\text{Pb}(\text{CH}_3\text{COO})_2$							
antimony trichloride $\text{SbCl}_3$							
calcium hypochlorite $\text{Ca}(\text{ClO})_2$							

alloy	Special metal		Nonmetal			Other
	Titanium	Zirconium	impervious graphite (19-22)	gum	thermoplastic resin	
Hastelloy						



中共廣東省委宣傳部



1997年1月31日 第1版第1刷发行

式サインツナ-71

Printed in Japan  
©1997

価格 20,000円 (税別)

神戶 船子 本日はお返事ありがとうございます。

[illegible]

「ULSI 生産技術緊急レポート」編集委員会

■顧問

水野 修	日本電気(株)ULSIデバイス開発研究所長
原 央	(株)東芝 研究開発センター 主席技監
牧本 次生	(株)日立製作所 常務取締役
安岡 晶彦	三菱電機(株)ULSI 開発研究所 所長
矢木 肇	ソニー(株)理事 中央研究所技師長

■編集幹事

吉川 公隆	日本電気(株)ULSI デバイス開発研究所 高集積技術開発部長
山本 真一	(株)東芝 半導体生産技術推進センター 生産技術企画担当部長
吉見 武夫	(株)日立製作所 半導体事業部 半導体技術開発センター 副技師長
平山 誠	三菱電機(株)ULSI 開発研究所 LSI プロセス開発第一部長
服部 毅	ソニー(株)超 LSI 研究所 主幹研究員

アンケート調査協力企業 (順不同)

日本電気(株)	(株)東芝	(株)日立製作所	三菱電機(株)	ソニー(株)	沖電気工業(株)
富士通(株)	三洋電機(株)	松下電子工業(株)	シャープ(株)	セイコーエプソン(株)	

以上11社

執筆者 (掲載順)

Kenneth Cadlan	Intel Corporation principal engineer in the Innovative Technology group
Seiichi Morimoto	Intel Corporation Senior Staff engineer at Portland Technology Development
Ara Philipossian	Intel Corporation Materials Technology Manager
Siva Sivaram	Intel Corporation Director of Engineering at IC procurement and enabling division
Yumiko Takamori	Intel Corporation Strategic Research / Planning Manager, TMG
Charles Hannes	IPEC Director of Corporate Marketing
Jim Valentine	STRASBAUGH Technical marketing Specialist
辻村 学	(株)荏原製作所 精密・電子事業本部技術統括部長
飯田 進也	スピードフナム(株)常務取締役
池田 健一	スピードフナム(株)CMP技術部長
熊谷 多賀史	アライドマテリアルズ(株)デバイス製品事業本部 CMP プロジェクト次長
宮入 広雄	三菱マテリアル(株)総合研究所マカトロ・生産システム研究所副主任研究員
Jan King	Cybeq Nano Technologies CMP プロセスプロジェクトマネージャー
綱田 雅文	東芝機械(株)半導体装置事業部 半導体装置部 主査
斎藤 日出夫	東芝機械(株)中央研究所第1研究部 SC 研主任
大倉 靖浩	住友金属工業(株)半導体装置事業部 CMP 開発プロジェクトチーム 担当課長
滝川 敏二	住友金属工業(株)半導体装置事業部 CMP 開発プロジェクトチーム 担当副長
別府 敏保	住友金属工業(株)半導体装置事業部 CMP 開発プロジェクトチーム 担当副長
南川 康夫	セキエック(株)半導体装置事業部 CMP 開発プロジェクトチーム 担当副長
山下 義典	大日本スクリーニング(株)電子機器事業本部多層製造部技術2課 係長 補佐
永徳 庸郎	ロデール・ニッタ(株)技術部 開発課 課長
寺崎 忠士	(株)フジミエレクトロニクス(株)商品開発部 商品開発課 主任
鈴村 聡	

目次

特別寄稿 Intel 社

Current Issues and Future Trends in Chemical Mechanical Polishing... 7

1. Polish Equipment .....	8
2. CMP Consumables .....	10
3. Oxide CMP Process .....	13
4. Conclusions .....	17

第1部 デバイスマーカのCMP実用化の実態とその概要

調査の狙いと要約 .....	21
アンケート調査結果 .....	24

第2部 量産適用のためのCMP装置、材料の現状と開発の方向性

1. 装置メーカー

1 IPEC / Current Status and Future Strategy of CMP Technology for IC's Production .....	81
---	----

2 STRASBAUGH / Strasbaugh CMP .....

1. Strasbaugh and CMP Today .....	84
2. Strasbaugh's Next Generation CMP Planer/Polisher and the Future .....	85
3. Other Developments .....	86
4. The Strasbaugh Company .....	87

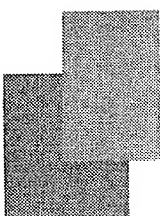
3 株式会社荏原製作所 / 量産適用のためのCMP装置 .....

1. CMPの歴史概観 .....	88
2. 図表による「量産適用のための装置」とは？ .....	89
3. クリーニング対策 .....	90
4. 洗浄機の一括化 .....	90
5. 高スループット化 .....	91
6. 消耗材コスト低減 .....	92
7. スラリーのリサイクル .....	92
8. 信頼性の向上 .....	92
9. 今後の課題 .....	92

4 スピードフナム株式会社 / 量産用CMP装置としての開発と今後の方向 .....

1. 装置概要 .....	94
2. プロセス .....	95
3. スループット .....	96
4. 信頼性 .....	97
5. ランニングコスト .....	97
6. 今後の方向 .....	98

5	フライイド マテリアルス ジャパン株式会社 /MIRRA™ CMP SYSTEM .....	99
1.	設計コンセプト .....	99
2.	装置の基本構成 .....	99
3.	装置の特長 .....	100
4.	出荷実績と今後の方向 .....	102
6	Cybeq Nano Technologies /量産適用のためのCMP装置、材料の現状と開発の方向性 .....	103
1.	CMP装置コンセプト .....	103
2.	プロセス性能 .....	107
3.	まとめ .....	114
7	東芝機械株式会社 / 枚葉式CMP装置 CMS-200 .....	115
1.	CMS-200の構成 .....	115
2.	CMS-200の機能 .....	116
3.	新技術へのアプローチ .....	117
4.	今後の動向 .....	119
8	住友金属工業株式会社 / 酸化膜用量産対応CMP装置SP4000 .....	120
1.	装置概要 .....	120
2.	SP4000のクリーン化対策 .....	122
3.	SP4000のプロセス性能と量産対応機能 .....	123
4.	COO 低減への取組み .....	124
5.	今後の開発計画 .....	125
II.	CMP 対応洗浄専用メーカ	
1	OnTrak Systems / 第2世代のCMP技術 .....	126
1.	CMPプロセス .....	126
2.	CMCプロセス .....	127
3.	3LPTプロセス .....	128
4.	第2世代のCMPプロセス .....	130
2	大日本スクリーン製造株式会社 / 量産適用のためのCMP後洗浄技術と装置 .....	131
1.	CMP後洗浄装置に求められること .....	131
2.	CMP後洗浄技術 .....	132
3.	まとめ .....	136
III.	材料メーカ	
1	ロデール・ニッタ株式会社 / CMP用消耗資材の現状と開発の方向性 .....	137
1.	CMP用消耗資材の現状 .....	137
2.	CMP用消耗資材の開発の方向性 .....	141
3.	まとめ .....	143
2	株式会社フジミインコーポレーテッド / CMPスラリーの循環使用 .....	144
1.	実験 .....	144
2.	結果 .....	146
3.	まとめ .....	149



## 特別寄稿

Intel 社

## Current Issues and Future Trends in Chemical Mechanical Polishing

# Current Issues and Future Trends in Chemical Mechanical Polishing

Kenneth Cadieu, Seichi Morimoto, Ara Philipossian, Siva Sivaram, Yumiko Takamori

---

This paper will concentrate on Intel's efforts at enabling multiple levels of metallization for microprocessors, using Chemical Mechanical Polishing (CMP). The paper addresses the issues and problems encountered in implementing CMP based processes, equipment, and consumables in volume manufacturing, concentrating on oxide polishing. Discussions on evolution in equipment configurations, the physical and chemical properties of the slurry, the mechanical properties of the pads, and the CMP process parameters are included in this paper.

## Introduction and overview

Logic technologies, and in particular devices that depend on a high packing density of randomly interconnected gates, rely intensely on many levels of metallization to achieve the density and performance goals. A typical example of such a device is the microprocessor. Over the last decade, the number of levels of metals in these devices has grown from two to over five. Achievement and control of narrow line widths for these metal lines presupposes a relatively flat topography which in turn enhances the ability to pattern, etch, and clean the metal lines. Large devices such as the microprocessor ( $> 150 \text{ mm}^2$  in area) require that such planarity is achieved over dimensions similar to the size of the lithographic imaging field.

It is thus evident that microprocessor technologies need a planarization technique that is not locally constrained (such as a gap fill or a plug), but rather a global planarity effector. Traditional planarization techniques available in semiconductor processing have depended on the flow of a viscous layer (i.e. photoresist spin followed by an etch back, or spun on glasses and dielectrics). All of these techniques provide very good local and intermediate range planarity (i.e. in the order of tens of micrometers). They are also pattern dependent, with planarity degrading away from an isolated edge. They provide little global planarization. Currently, the only planarization technologies that produce water scale planarity depend on chemical mechanical techniques where a stiff pad acts as a global planarity effector. This paper will concentrate on Intel's efforts at enabling multiple levels of metallization for microprocessors, using Chemical Mechanical Polishing (CMP).

In order to achieve a flat surface prior to each level of metallization, both the oxide and any local plugs need to be planarized. Dielectric polishing forms the basis of all interlevel CMP schemes. Dielectric polishing needs to include the first dielectric on polysilicon (usually a BPSG based sandwich), intermetal dielectrics (i.e. TEOS based plasma oxides), and, in some cases, the final passivation layers such as oxides, nitrides or oxynitrides. This paper addresses the issues and problems that Intel has encountered in implementing CMP based processes, equipment, and consumables in volume manufacturing of microprocessors.

# 1. Polish Equipment

During CMP, down force is applied to the wafer pressing it against the polishing pad. Slurry is pumped onto the pad, and the wafer and pad are rotated. This simplified view of CMP is shown schematically in Figure 1. The pressure of the wafer against the pad is critical to obtaining polish rate uniformity. In fact, controlled polish non uniformity can be used to correct for systematic non uniformity due to the pad/wafer interaction. Examples of this are curved carriers and back pressure. Pumping of slurries is difficult. Slurries tend to be corrosive and contain very fine particles that destroy moving parts such as bearings. It has been found that the optimal method of pumping slurry is to use a system that completely isolates the slurry from moving parts of the pump. Pumps such as peristaltic and dual diaphragm pumps work well. During polishing, both the pad and the wafer are rotated in the same or opposite directions. This applies large shear stresses to the wafers that tend to cause the wafer to slip out of the wafer carrier. A retaining ring made out of a wear resistant material is used to hold the wafer in place. Traditionally, the ring was fixed to the carrier.

Although polishing has been done on blanket silicon wafers for many years, the first fabrication (fab) compatible polisher did not appear until the late 1980's. The key characteristic that made this polisher fab compatible was robotic cassette to cassette capability (C to C). The first production tool was delivered in 1989. It had a single polish platen and a single polishing head. Wafers were held in the head by a fixed retaining ring. The tool had inherent problems related to the large size of the machine and the relatively low throughput rate for long polish steps. As the number of polish steps have increased in submicron IC processes, the large number of polishers required for manufacturing has become a major issue. Other competitive machines began to arrive on the market in 1990. The first of these consisted of two polish heads on a single large polish platen. The system had inherently higher throughput but also had a larger footprint. One innovation that these early tool vendors brought to CMP market was the use of pad conditioners. It had been discovered that during early tool vendors brought to CMP market was the use of pad conditioners. It had been discovered that during polishing the rate decreases due to pad glazing. Mechanically abrading the surface of the pad, either during polishing or between polishes, reduces the rate at which the rate drops. There are several novel designs for pad conditioners exemplified by the design disclosed by Intel<sup>1)</sup>.

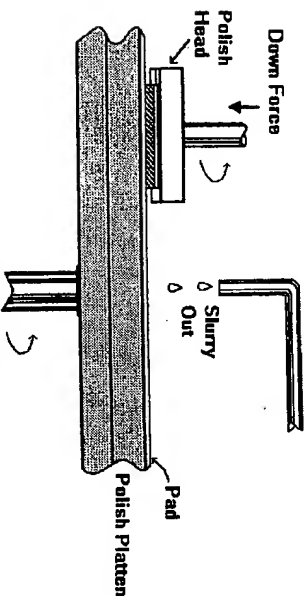


Figure 1. Schematic diagram of chemical mechanical polish

Table 1. Examples of polish tools available today based on number of polish heads.

Number of polish heads	Number of polish platens	Tool
1	1	A
2	1	B
4	3	C
4	4	D
5	1	E
6	1	F

\* Three heads are used for polishing at any time.

Today, most polishers are distinguishable by the number of polishing heads and the number of primary polish platens that each tool has. These features are summarized in Table 1 for several tools that are available today. The number of polish heads tells us the number of wafers that can be in process simultaneously. It is also an indication of increasing throughput. Machines in the middle rows represent compromises between high throughput, size, and complexity.

There are several innovations on the current generation of tools. For example, a method has been invented <sup>2)</sup> for applying differential pressure to the retaining ring to improve uniformity.

Systems have been developed that deliver slurry through the pad instead of on top of the pad, and move the wafer in an orbital motion <sup>3)</sup>. There are also polish systems where the polish table is not rigid, and an equal air pressure needs to be applied behind the pad and the wafer <sup>3)</sup>. In addition, in-situ endpoint systems have been developed that directly measure optical film thickness during polishing. Motor current techniques that measure friction at the wafer surface have also been used to endpoint polish.

There are several major challenges for the future generation of tools that will be emerging within the next year. These include automation, 300 mm wafers, and in-situ metrology. On the automation front, the development of fully integrated dry-in/dry-out polishing systems that improve throughput and reduce footprint.

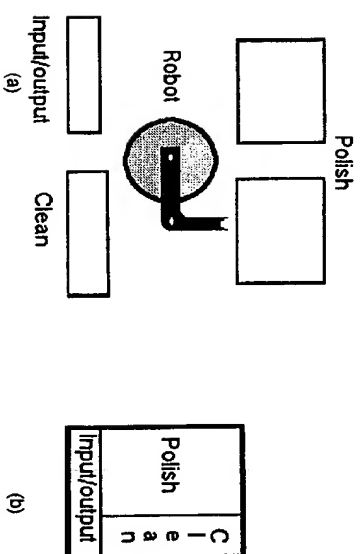


Figure 2. Schematic figure of linked (a) and integrated (b) polishing systems

Figure 2 shows schematically linked and integrated systems. In linked systems, discrete polishers, cleaners, and an input/output interface are linked by an external robot. The external robot moves cassettes of wafers between tools. While this system is large, it does reduce the number of people required to run the polish area, and eliminates possible ergonomic issues with polish and clean tools. In the integrated system, a supplier delivers a total solution to their customers. Within the tool, either cassettes or single wafers are moved between the polish and clean modules.

The transition from 150 to 200 mm wafers was fairly transparent to CMP tool suppliers, since existing tools could easily accommodate the larger wafer size. With 300 mm wafers, most machines will need to increase the frame of the polisher. Of particular concern will be wafer handling. 300 mm wafers are about four times heavier than 200 mm wafers.

One of the factors that impacts CMP throughput and floor space is the need for metrology tools. The drive in future tools is to incorporate in-situ metrology for device wafers into integrated tools with closed loop control. This will also limit process excursions to the wafers in process.

## 2. CMP Consumables

During CMP there are two primary consumables, slurry and pads. It has been discovered that in order to overcome a majority of the technical issues associated with oxide CMP, further fundamental understanding of the mechanism of oxide removal during the CMP process is essential. While several mechanisms have been proposed <sup>4) 5)</sup>, a comprehensive mechanism remains to be defined which links oxide removal rate to bulk attributes of slurries and pads such as:

- pH, viscosity, ionic strength and abrasive content of the slurry <sup>6)</sup>
- Slurry abrasive type, morphology, geometry and size distribution <sup>6)</sup>
- Buffers and other additives in the slurry
- Pad hardness, specific gravity and compressibility <sup>7)</sup>
- Pad morphology and texture

Table 2 summarizes the effect of tuned silica abrasive geometry on normalized oxide removal rate (RR) and within wafer non uniformity (WIWNU). In all cases, pH and solids content of the formulations have been kept constant. Neither primary particle size (PPS) nor mean aggregate size (MAS) seem to correlate with RR and WIWNU. This contradicts other reports <sup>8)</sup> and suggests that other factors are influencing RR. Actually, the data shows a direct correlation between RR and the ratio of PPS to MAS (Figure 3). It is believed that this ratio contributes to the physical component of the oxide CMP process since the higher the ratio, the lower the deformation of the abrasive under actual planarization conditions,

Table 2. Effect of abrasive geometry on oxide polish performance

Slurry	Appx. Primary Particle Size (nm)	Appx. Mean Aggregate Size (nm)	Normalized Mean Removal Rate	Normalized WIWNU (3-sigma)
A	28	122	86	—
B	29	110	100	100
C	19	95	82	83
D	20	110	79	154
E	50	200	94	104

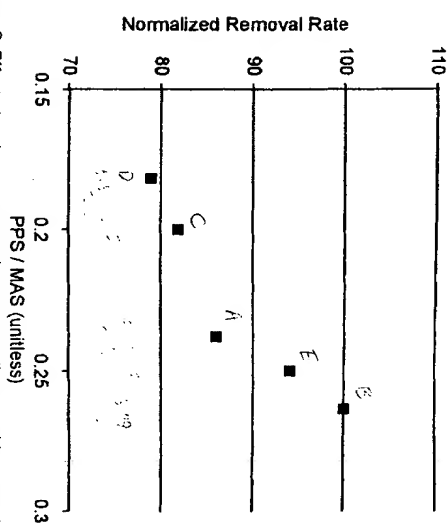


Figure 3. Effect abrasive geometry <(ie aspect ratio)> on oxide removable rate

and hence the higher the RR. The PPS to MAS ratio can therefore be thought of as a Deformation Factor (DF). This indicates that when defining tuned silica abrasives for optimal RR performance, DF, rather than individual aggregate and primary particle sizes, should be the parameter of interest. In Table 2, all five formulations resulted in statistically equivalent defect density and planarity on patterned wafers. Lack of a correlation between abrasive geometry (i.e. PPS, MAS and DF) and WIWNU is expected since WIWNU is a complex function of process and hardware parameters.

To effectively address the above technical issues, future trends need to include several core competencies, such as (1) flame synthesis and classification, (2) dispersion, mixing and filtration, (3) reaction kinetics, (4) electrochemistry, (5) colloid chemistry (6) surface chemistry, (7) thermodynamics, (8) fluid mechanics, (9) polymer chemistry and strength of materials, and (10) numerical analysis.

Lack of a fundamental understanding of the relationship between polish performance and pad and slurry attributes raises the question of whether current definitions of slurry and pad quality are accurate. In the absence of fundamentals, suppliers and IC manufacturers have resorted to the use of fragmentary data to define a list of critical slurry and pad parameters. This list is expected to grow as more data becomes available. One hopes that the number of critical factors will eventually decrease through consolidation into more fundamental and meaningful metrics.

Currently, the following parameters are generally specified or reported:

- For slurries – Viscosity, pH, abrasive content, shelf-life at room temperature, storage temperature range, package type, mean aggregate size, aggregate size distribution, maximum aggregate size gross anions/cations/hydrocarbons content, as well as trace cations content. Specifications for abrasives used in the slurry include type, adsorbed impurity content (i.e. chloride in the case of tuned silica), and pre-dispersed surface area.
- For pads – Thickness, specific gravity, adhesive strength (a potential ergonomic consideration during routine pad changes), compressibility and hardness.

Table 3. Effect of trace metals on oxide polish performance (PPM)

Slurry	[Al]	[Ca]	[Cr]	[Fe]	[Ni]	Normalized Defect Density
F	< 0.2	< 0.2	< 0.7	1	< 0.2	1
G	99	1.2	3	18	3.2	3 to 11

Table 4. Effect of trace metals on oxide polish performance

Slurry	Normalized Hydrocarbon Content	Normalized Defect Density
H	1	1
I	14	3 to 6

Specifying pH as a means of controlling slurry chemistry can be problematic since it may allow broad ranges in concentration of components in order to target pH. In the case of buffered formulations, this can cause large variations in buffer capacity which can ultimately affect RR. Therefore, additional parameters, such as conductivity, need to be specified to control slurry chemistry.

Physical properties of pads, such as specific gravity, are loosely correlated with pad performance <sup>8)</sup>. In particular, for most industries, hardness tests use a comparative scale rather than an absolute scale which is sometimes difficult to link with mechanical properties. More reliable tests, such as compressibility, are not well correlated with polishing parameters. Traditional mechanical property tests (i.e. elongation, compressibility and elasticity) which rely on macroscopic techniques, represent averages and are unable to capture the wide variation of properties from point to point within a pad <sup>9)(10)</sup>.

Table 3 summarizes the effect of trace metal levels in oxide slurry on defect density. There seems to be a direct correlation between metal content in slurry and defect density. While it is unclear which metals and at what levels begin affecting defect density, the data indicates the importance of performing trace metals analysis at suppliers' sites on every batch of slurry prior to shipment and imposing stringent requirements on trace metal levels. It should be noted that despite its high metal levels, formulation G resulted in statistically equivalent RR, WIWNU and planarity.

Table 4 summarizes the effect of hydrocarbon contamination in the oxide slurry on defect density. There seems to be a direct correlation between hydrocarbon content (in this case, the hydrocarbon was comprised of a highly polar group) and normalized defect density (mostly in the form of scratches). No differences in RR, WIWNU or planarity were found among wafers polished with Formulations H and I suggesting a problem with a "localized" rather than a "global" signature. Given the highly polar character of oxide slurry abrasives (i.e. Si-OH bonding), and the polar nature of the hydrocarbon, it is suspected that abrasive particles are attracted to the contaminant, forming a larger agglomerate, and resulting in local scratches.

Future trends in pad and slurry quality revolve around the need to:

- Drive analytical procedures, as well as packaging & temperature monitoring (for slurries only) standardization.
- Develop precise and accurate metrology procedures with routine calibration, and correlation requirements (i.e. tool to tool, site to site, operator to operator).

- Validate the key assumptions made in particle metrology and develop tools and procedures for rapid and reliable determination of abrasive characteristics in slurries.
- Develop material specifications based on comprehensive functional tests rather than perceived process needs. Correlate functional tests to analytical tests to assure quality at the suppliers' sites and to increase supplier accountability.
- Investigate the economics of performing selected quality checks on slurries and making needed modifications at point-of-use.

## 3. Oxide CMP Process

### 3.1 CMP Process Requirements and Issues :

Full planarization of oxide (inter-layer dielectric) layer is necessary for state of the art lithography due to the narrow range in depth of focus imposed by high numerical aperture lenses. CMP is the only technique with the capability for smoothing out topography over the millimeter range.

CMP, however, has been one of the most difficult processes to control within-wafer and wafer-to-wafer uniformity. Within-wafer uniformity is affected by wafer flatness, carrier pad material, carrier design, and pad conditioning method. Wafer edge profile can be distorted due to the discontinuity in pressure between wafer edge and carrier retaining ring. An effective pad conditioning process to constantly supply fresh slurry is required for repeatable wafer to wafer removal rate. Defect density reduction to remove slurry from wafer surface has also been a challenging task.

Planarity or planarization capability is another key feature of CMP process. Planarization capability can be defined by step height ratio (SHR) and planarization distance (PD) and as shown in Figure 4. The SHR is defined as the ratio of post-polish to pre-polish step height for a semi-infinite step and is used as a normalized measure of LLD oxide planarity. SHR is zero for the case of perfect full planarization and is one for the case of smoothing, but not a full planarization. For example, SOG (Spin-on-glass) planarization only smoothes out local variations in topography and does not create long range planarization, so it has an SHR of one. The SHR of CMP process can be anywhere from zero to one depending upon the polishing process, type of polishing pad, and the amount of material removed during polishing.

The PD is defined as the distance over which the planarization occurs. A longer PD is desirable since variations in topography over areas that are smaller than the PD will be planarized. The PD of a CMP process can be several hundred microns to several millimeters depending upon the polishing process. CMP process with small SHR and long PD will result in small within-die (WID) thickness variation.

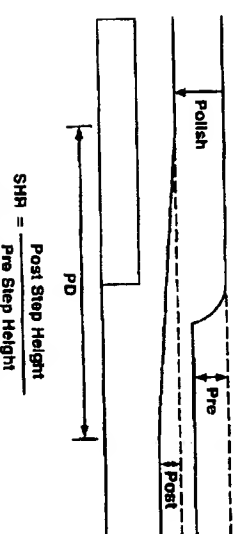


Figure 4. Definition of PD and SHR

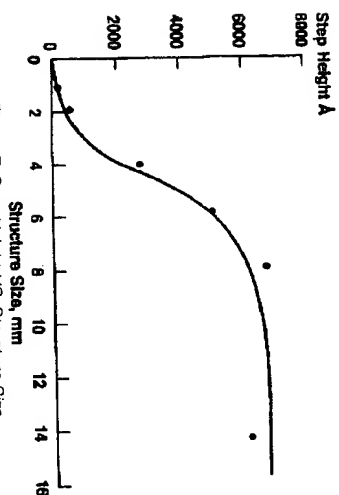


Figure 5. Step Height VS Structure Size

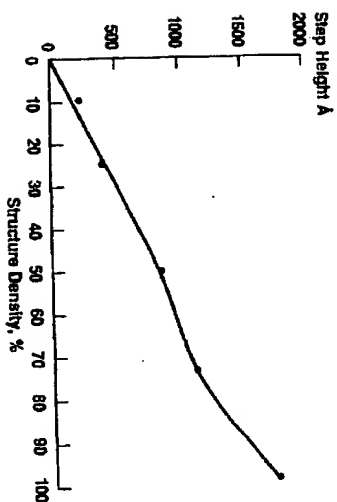


Figure 6. Density Effect

The WID uniformity depends upon the actual circuit topography and the SHR and PD. For example, the remaining oxide thickness (or step height) is greater on wider structures such as a wide metal pad and is less on isolated narrow lines as shown in Figure 5. The WID uniformity (and step height after polish) also depend upon the density of the underlying topography as shown in Figure 6. Areas with lower metal density polish faster than areas with dense underlying topography. Thus, each circuit design will have a slightly different WID nonuniformity, due to variations in the size and density of interconnects.

### 3.2 CMP Process Characteristics:

In addition to the factors outlined in Section 2, the following polish process parameters determine removal rate, within-wafer uniformity and SHR:

- Wafer down force pressure
- Platen rotational speed
- Carrier rotational speed
- Pad break-in and conditioning

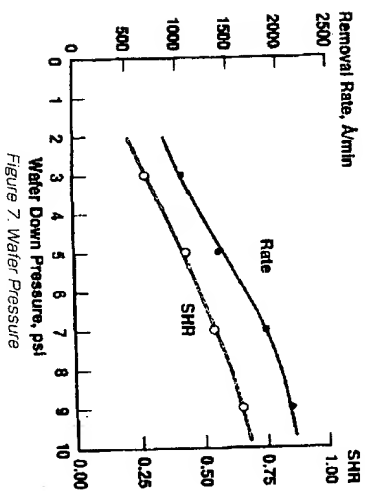


Figure 7. Water Pressure

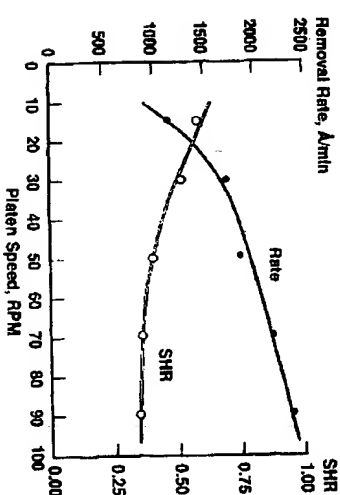


Figure 8. Platen Speed

Downforce pressure is one of the key parameters which affects removal rate and SHR. Higher water pressure applied to the polish pad increases the removal rate almost linearly, as shown in Figure 7. The SHR also increases with increasing polish pressure. Apparently, at high polish pressures the pad contacts more of the valley regions of the topography. At lower pressures the pad contacts mainly the hill regions. The WIW uniformity is not significantly affected by the polish pressure.

Platen speed is another parameter which affects the removal rate and SHR. The oxide removal rate is directly correlated to the platen speed, as shown in Figure 8. The removal rate increases as platen speed increases, especially at lower rotational velocities. The SHR is inversely related to the platen speed because at higher speeds the pad contacts mainly the hill regions of the topography. The pad does not have sufficient time to conform to the valley regions. The WIW uniformity is generally adversely affected by platen speed.

Carrier rotation speed has no significant effect on changing the center to edge uniformity in the lower carrier speed range of 15-50 RPM, as shown in Figure 9. This is because the diameter of the carrier is much smaller than that of the platen, and therefore the linear velocity created by carrier rotation is much lower than that created by platen rotation. At carrier speeds above 70 RPM, however, the linear speed of the carrier becomes comparable to that of the platen. As a result, removal rate on the edge of the wafer increases relative to the center of wafer.



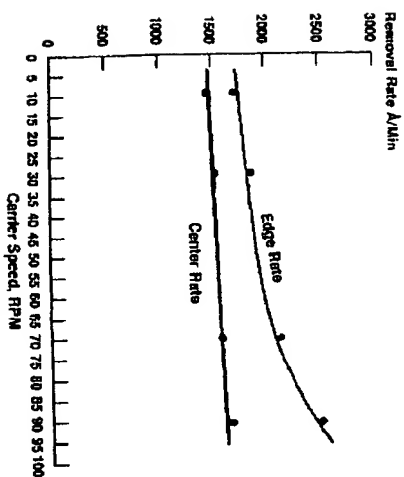


Figure 9. Center and Edge Rate VS. Carrier Speed

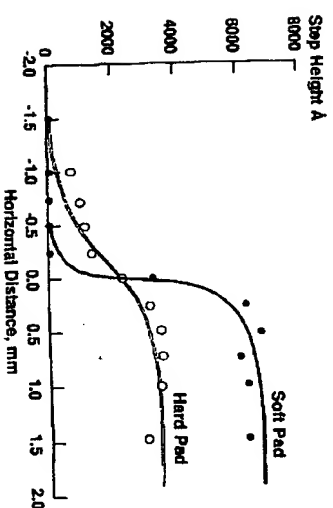


Figure 10. Step Profile After Polish-Soft vs. Hard PAD

The step profile after polish is shown for different pad types in Figure 10. A harder (less compressible) pad gives lower SHR and longer PD which leads to improved within-a-die (WID) thickness uniformity but worse within-a-wafer (WIW) uniformity. Therefore, there is a tradeoff between improvements in WID uniformity and WIW uniformity.

A new polish pad requires a break-in procedure prior to processing wafers. The purpose of the break in is to clean and condition the pad surface to establish a stable polish rate. The pad also needs to be conditioned after polishing each wafer in order to restore the original form, free of surface residue build up and glazing. Without conditioning, the polish rate drops over time, resulting in rework, a loss of wafer throughput and increased equipment downtime for pad changes. A properly conditioned pad maintains a stable removal rate and maximizes the pad lifetime. Figure 11 shows the example of rate stability with and without conditioning between each wafer.

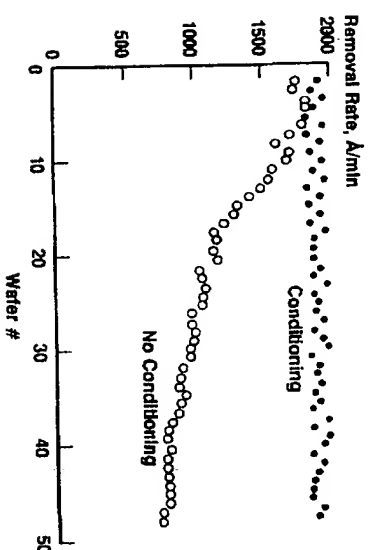


Figure 11. PAD Conditioning Effect

## 4. Conclusions

This paper summarized in general terms the progress that has been made in the field of global planarization using chemical mechanical polishing. The paper concentrated on oxide polishing. Evolution in equipment configurations that optimized through-put, within and wafer to wafer non-uniformities and manufacturability was discussed. The consumable set that goes along with the equipment still needs extensive characterization. Clear correlations of process parameters to the physical and chemical properties of the slurry and the mechanical properties of the pads need to be established to minimize the manufacturing variability induced by the consumables. In order to achieve good step height reduction and SHR, parameters that deal with the equipment (such as down force, platen and carrier speeds), consumables (such as solids content, size and distribution of particles, and pad mechanical properties), and their interaction need to be evaluated.

For the volume manufacturing of large logic devices such as the microprocessor, careful study of the equipment, consumable, and process parameters is needed to optimize interlevel planarity. Intel has developed these processes for successive generations of microprocessors to achieve high manufacturing yield and improved device performance.

## Acknowledgments

The authors would like to thank Intel Fellows, Dr. Leo Yau and Dr. Paolo Gargini, for giving us support and reviewing this paper.

#### References

1. J. R. Breivogel, L. R. Blanchard, and M. J. Price, "Polishing Pad Conditioning Apparatus for Wafer Planarization Process", U. S. Patent #5,216,843, June 8, 1993.
2. N. Shenden, K. C. Struven, and R. J. Kolenkow, "Wafer Polisher Head Having Floating Retainer Ring", U. S. Patent # 5,205,082, April 27, 1993.
3. J. R. Breivogel, S. F. Louke, M. R. Oliver, L. D. Yau, C. E. Barnes, "Orbital Motion Chemical-Mechanical Polishing Apparatus and Method of Fabrication", U. S. Patent # 5,554,064, September 10, 1996.
4. Patrick et. al., "Application of Chemical Mechanical Polishing to the Fabrication of VLSI Circuit Interconnections" J. Electrochem. Soc., Vol. 138, p.1778, 1991.
5. Cook, J. Wang, D. James and A. Sethuraman, "Semiconductor International", p.141, Nov. 1995.
6. Scherber and M. Neville, "Proceedings of the Symposium on Planarization Technology", CMP, Semicon West, 1994.
7. Jastrah, et. al., "Chemical and Mechanical polishing: Process Manufacturability", Solid State Technology, p.71, July 1994.
8. Hayashi, "Proceedings 24th Symposium on ULSI, Ultra Clean Technology Tokyo", p.182, March 1995.
9. Tomozawa et. al., "Effect of Pad Characteristics on Oxide Polishing Performance", SRC Topical Conf. in CMP, July 1995.
10. Jeong, T. Karaki-Doy et. al., "New polishing by mechanical and chemical polishing techniques insensitive to pattern-topography for VLSI wafer", "Proceedings of MicroProcess", p.121, 1994.

## 第 1 部

### デバイスメーカーのCMP実用化の実態とその概要

1 UNITED STATES DEPARTMENT OF COMMERCE  
2 PATENT AND TRADEMARK OFFICE  
3

4 Applicant : Shigetoyo Matsumura )  
5 Serial No. : 09/761,043 ) ART UNIT: 1712  
6 Filing Date : January 15, 2001 ) EXAMINER:  
7 Title : Colloidal Silica Slurry ) Daniel S. Metzmaier

8 Commissioner of Patents and Trademarks  
9 Washington, D.C. 20231

10 For: Colloidal Silica Slurry  
11

12 DECLARATION  
13

14 I, Masatoshi Sakai, hereby declare as follows.  
15

16 1. I was born on January 24, 1949, in Nanao city, Ishikawa prefecture, Japan,  
17 and was graduated from Yokohama National University, Faculty of  
18 Engineering on March, 1971. My major while I was studying at Yokohama  
19 National University was safety engineering.  
20

21 After graduating from Yokohama National University, I had worked  
22 research and development of colloidal silica in Tonen Corporation since 1985,  
23 and thereafter, I have worked research and development of colloidal silica in  
24 Fuso Chemical Co., Ltd.,  
25

26 2. I am one of the inventors of Colloidal Silica Slurry, and have a full  
27 knowledge of the content thereof.  
28

1 3. I have examined the documents cited by the examiner, i.e., U.S. Patent No.  
2 3,860,431 and U.S. Patent No. 5,230,833.

3  
4 (1) In the U.S. Patent No. 5,230,833 (hereinafter referred to as '833), a low  
5 metal silica slurry used in polishing of silicon wafer and a low metal silica is  
6 manufactured from silicate ester are described. In the column "BACK  
7 GROUND OF THE INVENTION", it is described that in the U.S. Patent No.  
8 3,860,431 (hereinafter referred to '431), hydrogen peroxide is used biocide of  
9 silica.

10 (2) In the '431 described as related art in the column of the "BACK GROUND  
11 OF THE INVENTION" of '833, hydrogen peroxide is exemplified as biocide.  
12 However, in '431, hydrogen peroxide is exemplified, but an invention which  
13 relates to the '431, hydrogen peroxide cannot be used as biocide.

14 The reason is that in the invention which relates to the '431, silica sol of  
15 basic pH is used. In '431, hydrogen peroxide is exemplified as biocide, but  
16 with silica sol of basic pH and less purity, hydrogen peroxide decomposes  
17 very easily.

18 From a result of test example described below, it is clear that hydrogen  
19 peroxide decomposes in silica sol of basic pH and less purity. That is, when  
20 hydrogen peroxide was added to silica sol which relates to the present  
21 invention which pH is neutral, no decomposition of hydrogen peroxide was  
22 confirmed. On the other hand, when hydrogen peroxide was added to silica  
23 sol of basic pH and less purity, decomposition of hydrogen peroxide was  
24 confirmed.

25  
26 (3) Therefore, hydrogen peroxide is exemplified in '431 as a kind of biocide,  
27 but hydrogen peroxide cannot be used substantially in an invention which  
28 relates to the '431. If hydrogen peroxide is used as biocide in the invention

1 which relates to the '431, hydrogen peroxide decomposes and does not work  
2 as biocide. Further, if hydrogen peroxide is utilized as biocide with the  
3 knowledge of decomposition of hydrogen peroxide, a considerable amount of  
4 hydrogen peroxide is needed. A large quantity of hydrogen peroxide causes  
5 corrosion to metal in utilization.

6 Further, in an invention which relates to the invention '833 which cites  
7 description of '431, in lines from 34 to 35 of eighth column of '833, pH of  
8 colloidal silica is described as alkaline, hence it is understood that also in an  
9 invention which relates to the '833, hydrogen peroxide cannot be used as  
10 biocide.

11  
12 (4) As explained above, in the inventions which relate to the '431 and '833, in  
13 specification, hydrogen peroxide is exemplified biocide of silica sol, but  
14 hydrogen peroxide cannot be used practically as biocide.

15  
16 4. I will describe hereinafter a test example to prove my view mentioned in  
17 the above.

#### 18 19 TEST EXAMPLE

##### 20 I. Purpose of test

21 To test degradation of hydrogen peroxide in colloidal silica prepared  
22 neutral zone and alkaline zone.

##### 23 24 II. Sample

25 As sample, PL-3 (product name) which is colloidal silica of ultra high  
26 purity manufactured by Fuso Chemical Co., Ltd., LUDOX HS-40 (product  
27 name) and LUDOX AS-40 (product name) which is colloidal silica  
28 manufactured by E.I. du Pont de Nemours and Company are used. Table 1

shows physico-chemical properties of each sample.

Table 1

Manufacturer Product name	Fuso Chemical Co., Ltd. Quartron PL-3	DuPont LUDOX HS-40	DuPont LUDOX AS-40
pH	7.3	9.6	9.2
density (20/4 centigrade)	1.120	1.300	1.290
concentration of silica wt%	19.51	40.76	40.64
BET specific surface area m <sup>2</sup> /g	77	182.4	122.8
primary particle diameter (specific surface area conversion method) nm	35.4	15.0	22.2
metal impurity			
Na ppm	0.03	4500	1000
K ppm	less or equal 0.01	5.2	2.5
Fe ppm	less or equal 0.005	69	60
Al ppm	less or equal 0.01	1.6	1.3
Ca ppm	0.02	13	7
Mg ppm	less or equal 0.01	10	4
Ti ppm	less or equal 0.5	27	27
Ni ppm	less or equal 0.005	0.05	less or equal 0.03
Cr ppm	less or equal 0.005	0.22	0.17
Cu ppm	less or equal 0.005	3	2

### III. Test method

30% of hydrogen peroxide was added to each sample and they were maintained at 40 centigrade and at room temperature. Then, concentration of hydrogen peroxide was measured at the start of test and the end of test.

Quantitative analysis of hydrogen peroxide was iodometric titration method that potassium iodide was added to the each sample and generated

Iodine is titrated with sodium subsulfite solution.

#### IV. Result

A result of sample maintained temperature conditions at 40 centigrade is shown in Table 2, and a result of sample maintained temperature conditions at room temperature is shown in Table 3.

Table 2

(ppm wt/wt)

	Before test	40 centigrade After 12 hours	40 centigrade After 12 days
Fuso Chemical Co., Ltd PL-3 +H <sub>2</sub> O <sub>2</sub>	138	138	138
DuPont LUDOX +H <sub>2</sub> O <sub>2</sub>	194	177	66.1
DuPont LUDOX +H <sub>2</sub> O <sub>2</sub>	160	158	92.7

Table 3

(ppm wt/wt)

	Before test	Room temperature 20-25 centigrade After 12 hours	Room temperature 20-25 centigrade After 12 days
Fuso Chemical Co., Ltd PL-3 +H <sub>2</sub> O <sub>2</sub>	138	-	137
DuPont LUDOX +H <sub>2</sub> O <sub>2</sub>	194	-	135
DuPont LUDOX +H <sub>2</sub> O <sub>2</sub>	160	-	139

#### V. Conclusion

As shown in table 2 and 3, in samples of neutral pH and ultra high purity, no decomposition of hydrogen peroxide was observed neither at 40 centigrade nor at room temperature.

On the other hand, samples of basic pH and less purity, decomposition of hydrogen peroxide was observed both at 40 centigrade and at room

1 temperature.

2 Therefore, it is understood that with colloidal silica slurry of neutral pH  
3 and ultra high purity, hydrogen peroxide can be utilized at 5 ~ 100 ppm as  
4 biocide for the colloidal silica slurry, but hydrogen peroxide cannot be used  
5 for colloidal silica slurry of basic pH and less purity.  
6

7 5. I further declare and certify that statements made herein are based on  
8 first hand and personal knowledge of the foregoing, except where indicated  
9 as being based on information and belief, and that if called to testify to the  
10 same, I would and could competently do so. I declare and certify that the  
11 foregoing is true under penalty of perjury of the law of the United States of  
12 America.  
13

14 Executed this 3/ day of January, 2003

15  
16 Masatoshi Sakai

17 Masatoshi Sakai  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28